Evaluation of the Sorption Process for Imidacloprid and Diuron in Eight Agricultural Soils from Southern Europe Using Various Kinetic Models

J. D. Fernández-Bayo,* R. Nogales, and E. Romero

Department of Environmental Protection, Estación Experimental del Zaidín (CSIC) C/ Profesor
Albareda 1, 18008-Granada, Spain

Kinetic studies are of great concern for understanding the processes and parameters involved in the sorption of pollutants by soils. Sorption kinetics of imidacloprid and diuron in eight soils of different characteristics, with very low organic carbon content were investigated. Pseudosecond-order kinetic reactions closely correlate with the experimental kinetic ($R^2 > 0.98$) in all soils. The sorbed amount of diuron was higher than that for imidacloprid. The low OC content of these soils correlated neither with the sorbed amount nor with the kinetic parameters for both pesticides. Imidacloprid sorption was correlated with silt and sand content and cation exchange capacity (CEC); meanwhile for diuron, no correlation was found. Thus, sorption kinetics take place throughout different mechanisms related mainly to the chemical character of the pesticides. Sorption kinetic parameters determined using three of the four models selected (pseudosecond-order kinetic reactions, Elovich equation, and Weber–Morris models) have been shown to be worthy to distinguish the process controlling the sorption kinetic of both pesticides.

KEYWORDS: Soil; sorption kinetic; imidacloprid; diuron; texture; organic matter; surface area; modeling

INTRODUCTION

Sorption is the most promising option for removing organic compounds from aqueous streams and for controlling their behavior in soils (*1*). The sorption of pesticides in soils has been studied in apparent equilibrium systems at constant temperatures (*2, 3*). However, the pesticide-sorbent reaction may require days, weeks, or months to raise the equilibrium levels (*4*). The sorption kinetic is important since it controls the efficiency of the process. The literature presents various mathematical models where pesticide sorption has been treated as first-order processes, pseudofirst-order processes, and so forth (*5*) in order to recognize the time required to reach equilibrium, to investigate the mechanisms involved, and to identify the sorption type and matrix sorption capacity as well as the order and rate of the reaction (*6*). The sorption process, which is usually rapid initially and slows down later until it reaches the equilibrium stage, can be divided into three stages. The first stage is associated with the diffusion of the pesticide to the sorbent's surface, which is called film mass transfer or boundary diffusion of solute molecules. The second stage, known as particle diffusion, is a slower process because of the diffusion of the solute within internal mesopores, micropores, or capillaries of the sorbent's internal structure, except for small sorbed amounts that appear on the external surface. The third stage is the sorption of the solute in the interior surface of the sorbent through mass-action-controlled mechanisms where a rapid uptake occurs (*5, 7, 8*).

Sorption of some pesticides has also been shown to increase with the aging of soil residues (*9–11*). This phenomenon affects the distribution of chemicals within sorption sites and may lead to unexpected persistence of these compounds in the environment and a decrease in the potential risk of leaching to deeper layers (*12*). This increment in sorption with time has been related to the pesticide sorption kinetic and diffusion processes. For these reasons, kinetic studies are of great interest in understanding the mechanisms related to the situation and persistence of chemicals in the soil. These studies are also important because the simulation models use sorption parameters to predict the location of pesticides in the field and in the registration process because of the high sensitivity of these models to sorption parameters (*1*). Some of the discrepancies found between the simulated fate with the theoretical model and pesticide behavior in the field may be related to the sorption kinetics and diffusion processes of these chemicals in the soil. However, relatively few studies relating to the sorption kinetic of pesticides in soils can be found (*6, 13–15*).

The objective of this work is to study the sorption kinetics of imidacloprid and diuron in eight different agricultural soils with low organic carbon (OC) content from Spain. This type of soil is common in southern Europe where 74% of this agricultural area is made up of soils with less than 2% OC content in the top soil (*16*). Different kinetic models were

* To whom correspondence should be addressed. Estación Experimental del Zaidín (CSIC), C/ Profesor Albareda 1, 18008-Granada, Spain. Tel: 0034 958 181600, ext. 126. Fax: 0034 958 129600. E-mail: jesus.bayo@eez.csic.es.
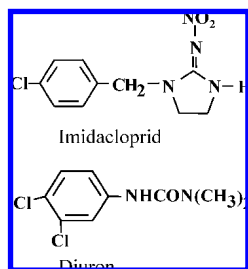
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Figure 1. Pesticide molecules.

Table 1. Soil Characteristics

soil	sand−silt−clay %	OC %	pH	CEC cmol$_c$ kg^{-1}	surf.[a] area m^2 g^{-1}
S1	84-10-6	0.26	7.9	4.51	13.4
S2	70-17-13	0.36	6.0	12.86	49.5
S3[b]	14-51-35	0.93	8.2	28.77	127.0
S4	64-14-22	0.24	5.4	13.82	57.9
S5	29-54-17	0.89	8.2	12.28	37.9
S6[c]	10-35-55	1.15	7.5	12.85	86.6
S7	47-34-19	0.78	5.9	22.61	71.7
S8	74-13-13	2.50	5.6	20.54	42.5

[a] Surface. [b] Dominant exchangeable cation in S3 is Ca^{2+} (43.35 cmol$_c$ kg^{-1}). [c] The carbonate content in S6 is 40.08%.

applied to determine the kinetic parameters, sorption mechanisms, and the potential rate-controlling stage. Two commercial formulations of imidacloprid, a systemic chloronicotinic insecticide, and diuron, a phenylurea herbicide, commonly used in southern Europe in both greenhouse and field crop systems, were selected.

MATERIAL AND METHODS

Chemicals. Confidor 200 SL 20% w/v (Bayer) is the commercial formulation of imidacloprid (1-[(6-chloro-3-pyridinyl) methyl]-*N*-nitro-2 imidazolidinimine), with a water solubility of 610 mg L^{-1} and K_{ow} of 3.72 (20 °C). Diurokey 80% w/w (Industrial Chemical Key S.A) is the commercial formulation of diuron (*N*′-(3,4-dichlorophenyl)-*N*,*N*-dimethylurea), with a water solubility of 42 mg L^{-1} and K_{ow} of 700 (25 °C) (**Figure 1**) (*17*). Previous assays did not show differences in sorption behavior when active ingredients were used; some data are already published (*18*).

Soils. Eight agricultural soils, with different characteristics, from the provinces of Jaen (S$_1$, S$_2$, S$_3$, and S$_4$), Granada (S$_5$ and S$_6$), Murcia (S$_7$), and Pontevedra (S$_8$) were used. Soil properties (**Table 1**) of the samples from the first 20 cm, which were air-dried and sieved (<2 mm sieve), were determined following validated official methods (*19*). Surface area was determined using the Keeling method (*20*). Mineralogy of the soil samples was investigated by X-ray diffraction (XRD) using an Analytical X'Pert Pro diffractometer equipped with an X'Celerator detector. Experimental conditions were fixed at 45 kV and 40 mA for Cu Kα radiation. Bulk sample patterns were recorded in powder mounts and clay fraction patterns in oriented mounts.

Kinetic Studies. Duplicate 5 g soil samples were placed in 25 mL glass tubes and mixed with 20 mL of an aqueous standard solution containing diuron and imidacloprid at 2.5 mg L^{-1}. The tubes were shaken at 15 ± 1 °C on a rotary shaker for 10, 20, and 40 min, and for 1, 2, 6, 12, 24, 48, and 72 h, and centrifuged at 1811*g* for 20 min at 15 °C. The supernatant was analyzed using High Performance Liquid Chromatograph (HPLC) as described below. The standard solutions containing the pesticides were run in parallel for control purposes. Blanks without pesticides were used for each sample. The sorbed pesticide amounts were calculated on the basis of the difference between the supernatant concentration in each sample and the control solutions.

Chemical analysis. A High Performance Liquid Chromatograph (HPLC) Series 1100 (Agilent, Germany) equipped with a diode-array detector was used. An analytical column (Zorbax Rx-C8 150 × 2.1 mm i.d.) packed with diisopropyl *n*-octyl (5 μm) and an Eclipse XDB-C8 (12.5 × 2.1 mm i.d.) guard cartridge packed with the same material were used. The operating conditions are described elsewhere (*21*). Aqueous samples were passed through 0.45 μm polytetrafluoroethylene (PTFE) filters (PALL, Life Sciences) for analysis.

Sorption Kinetic Models. *Hiperbolic Model.* This model in its linear form (eq 1) allows us to work out some sorption parameter values by adjusting it to the experimental data:

$$\frac{1}{q_t} = \left(\frac{B}{q_{max}} \times \frac{1}{t} \right) + \frac{1}{q_{max}} \tag{1}$$

where q_t is the sorbed quantity (μg g^{-1}) at time t, q_{max} (μg g^{-1}) is the maximum sorbed amount, t is the solid−solution contact time (h), and B is an empirical constant.

Pseudosecond-Order Kinetic Reaction Model. This model considers that sorption capacity could be proportional to the number of active sites occupied on the soil (eq 2):

$$\frac{dq}{dt} = k \cdot (q_{max} - q_t)^2 \tag{2}$$

where q_t and q_{max} were defined as in the hyperbolic model, and k is the reaction-rate constant (μg g^{-1} min^{-1}). Separating the variable in eq 2, integrating it with the appropriate boundary conditions, and rearranging the terms, the following linear equation was obtained:

$$\frac{t}{q_t} = \frac{1}{k \cdot q_{max}} + \frac{t}{q_{max}} \tag{3}$$

Elovich Equation. This equation considers that the sorption kinetic takes place in two phases: a fast initial reaction associated with the movement of the pesticide to the most accessible parts of the sorbent followed by a slower reaction due to particle diffusion in and out of the sorbent's micropores (*6, 22*). The linear form is written as follows (eq 4):

$$q = \frac{1}{Y} \ln(X \cdot Y) + \frac{1}{Y} \ln t \tag{4}$$

where q is the sorbed quantity, in μg g^{-1}, at time t, and X and Y are constants from the experiment carried out. The intercept [$1/Y \ln(X \cdot Y)$] coincides with the sorbed quantity (μg g^{-1}) during the fast phase, which was considered as the amount of pesticide adsorbed in 1 h, while the slope ($1/Y$) represents the slow sorption related to the duration of the second phase (*23*).

Weber−Morris Model. This equation considers that most of the sorption processes vary proportionally with $t^{1/2}$ (eq 5).

$$q = k \cdot t^{1/2} + C \tag{5}$$

In line with the other models, q (μg g^{-1}) is the amount of pesticide adsorbed per unit mass of soil at time t, where C is the intercept (μg g^{-1}), and k is the intraparticle diffusion rate constant (μg g^{-1} min$^{-1/2}$).

Statistical Analysis. The results were statistically analyzed using Statgraphic Plus 5.1. (Statistical Graphics Corp, Princeton, NJ).

RESULTS

Sorption Kinetics. Sorption of imidacloprid and diuron by eight agricultural soil samples at different contact times was carried out (**Figure 2**). For both pesticides, sorbed amounts increased rapidly during the first minutes of solid−solution contact time, followed by much slower progress toward an apparent equilibration. In all soils, apparent equilibrium was reached within 6 h and then remained almost constant or showed slight increments. Nevertheless, during the initial contact time (from 0 to 1−2 h), the increments in the sorption of imidacloprid were smaller than those of diuron, especially in the case of S1, S2, and S4 soils, indicating that diuron sorption is more time-dependent. This dependency was also found by Nkedi-Kizza (*24*). Soil samples also showed larger sorption capacity for diuron, indicating greater affinity for this more hydrophobic
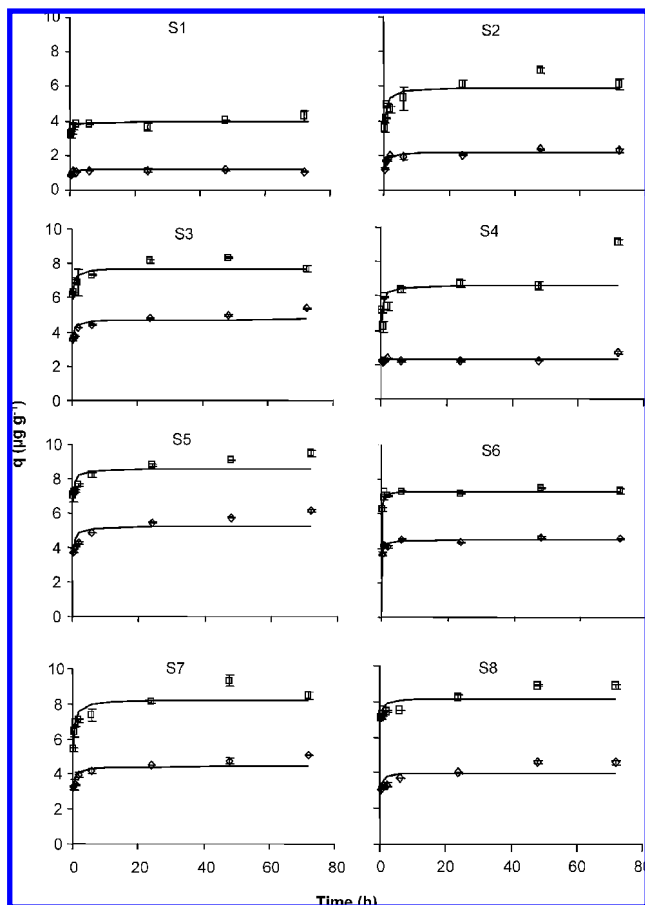
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Figure 2. Sorption kinetics of imidacloprid ($\diamond$) and diuron ($\square$) in the 8 soils. Symbols represent the experimental data, and lines represent the theoretical curves described by the hyperbolic model.

Table 2. Sorption Parameters from the Hyperbolic Model and Pseudosecond-Order Reaction Equation Applied to Express the Sorption Kinetics of Imidacloprid and Diuron on Eight Soils

	imidacloprid						diuron					
	hyperbolic model		pseudosecond-order reaction				hyperbolic model		pseudosecond-order reaction			
soil	$q_{max}{}^a$	R^2	$q_{max}{}^a$	$k^b \times 10^{-3}$	R^2		$q_{max}{}^a$	R^2	$q_{max}{}^a$	$k^b \times 10^{-3}$	R^2	
S1	1.20	0.80	1.36	8.9	0.98		3.95	0.76	4.22	5.2	0.99	
S2	2.17	0.93	2.30	9.8	0.99		5.91	0.87	6.55	6.9	0.99	
S3	4.73	0.74	5.29	3.7	0.99		7.69	0.76	7.88	50.2	0.99	
S4	2.32	0.11	2.57	5.9	0.98		6.63	0.44	8.31	1.0	0.98	
S5	5.24	0.72	6.07	2.7	0.99		8.60	0.70	9.40	2.9	0.99	
S6	4.49	0.85	4.59	15.6	0.99		7.32	0.87	7.31	128.1	0.99	
S7	4.44	0.73	4.97	3.6	0.99		8.22	0.89	8.80	3.3	0.99	
S8	4.00	0.63	4.53	4.3	0.99		8.19	0.55	8.96	3.1	0.99	

[a] q_{max} units in μg g^{-1}. [b] k units in g μg^{-1} min^{-1}.

pesticide. In order to investigate the sorption process, kinetic parameters, and the sorption rate-controlling stage, different kinetic models were applied to experimental data.

Hyperbolic Model. This empirical model was previously applied to the study of the sorption of picloram and cyanazine by soils (*25, 26*). The determination coefficients (R^2), used to evaluate the appropriateness of fit, were low for imidacloprid and diuron (**Table 2**), with the lowest values ($R^2 < 0.70$) found for soil samples S4 and S8. The lack of fit for both pesticides could be related to the sorption increment observed during the solid−solution contact time (**Figure 2**). When a shorter contact time was considered (24 h), the R^2 values actually increased. Thus, for soil sample S1, R^2 values for imidacloprid and diuron
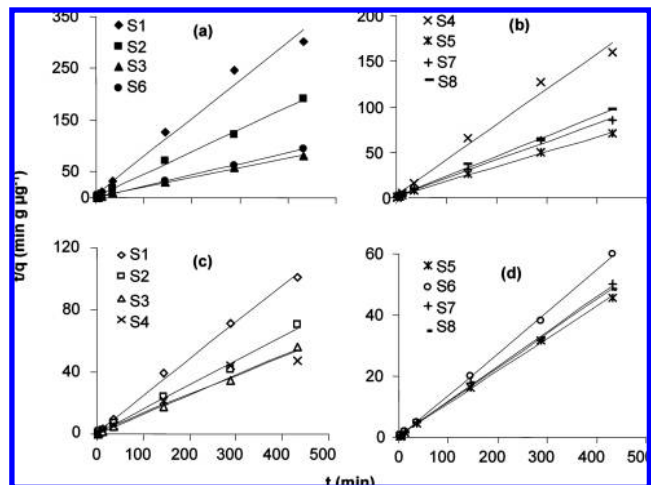

Figure 3. Pseudosecond-order sorption parameters of imidacloprid (**a** and **b**) and diuron (**c** and **d**) in the eight soils.

rose from 0.80 to 0.94 and from 0.76 to 0.81, respectively. However, for soil sample S4, with low OC content and the lowest R^2 value, a reduction in the solid−solution contact time did not improve R^2 values. Consequently, the hyperbolic model cannot explain the sorption kinetics of imidacloprid and diuron in the eight soil samples over the whole range of contact times.

Pseudosecond-Order Kinetic Reaction. Taking into account the previous results and assuming that sorption capacity could be proportional to the number of active sites occupied on the soil, this model was applied. The representation of t/q_t versus t (**Figure 3**) allowed us to work out q_{max} and k values from the slope and intercept, respectively (*27*). The pseudosecond-order reaction fairly accurately described the experimental data, with R^2 values of over 0.98 (**Table 3**). Values of q_{max} were slightly higher than those obtained with the hyperbolic model but displayed larger variations for diuron.

There was no correlation between q_{max} for imidacloprid and the OC content (**Figure 4a**). Nevertheless, three different groups were observed. The first group, with the lowest q_{max} and lowest OC values, corresponded to S1, S2, and S4 soil samples (sorbed amount of imidacloprid ranged from 10% to 25%). The second group, with higher q_{max} values and a sorbed rate of 40−50%, corresponds to soil samples with higher OC content (S3, S5, S6, and S7 soil samples). In the third group, with the highest OC content, is the sandy loam soil sample S8, where the q_{max} value was lower than could be expected given its OC content of 2.5%. This could be attributed to its high sand content or to the different nature of its OC. The q_{max} values for imidacloprid significantly correlated with silt content ($r = 0.84$, $P < 0.01$) and was inversely related to sand content ($r = 0.74$, $P < 0.05$) (**Figures 4b** and **c**). A relatively close correlation between q_{max} values and cation exchange capacity (CEC) of the soils was obtained ($r = 0.97$; $P < 0.01$) except for the S5 and S6 soils, which had a higher sorption capability than those expected, given their CEC values (**Figure 4d**).

The kinetic rate constants (k) for imidacloprid and diuron were different (**Table 2**). The highest sorption rate constant (k) for imidacloprid corresponds to the clay soil S6 ($k = 15.6 \times 10^{-3}$ g μg^{-1} min^{-1}). The lowest k values were found in S3, S5, S7, and S8 soil samples ($k < 5 \times 10^{-3}$ g μg^{-1} min^{-1}), with OC contents close to or higher than 1%. Intermediate k values correspond to S1, S2, and S4 soil samples with very low OC content ($<0.36\%$). A significant inverse correlation was observed between the reaction rate constant k and q_{max} values

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Table 3. Elovich Equation Parameters, Determination Coefficients (R^2) and Percentages of Imidacloprid and Diuron Sorbed in the Fast Phase by the Soil Samples

soil	imidacloprid				diuron			
	$[(1/Y) \ln(X \cdot Y)]$ (μg g^{-1})	%[a]	$1/Y$	R^2	$(1/Y) \ln(X \cdot Y)$ (μg g^{-1})	%[a]	$1/Y$	R^2
S1	0.99	87	0.07	0.75	3.52	97	0.14	0.72
S2	1.64	81	0.16	0.84	4.42	72	0.51	0.90
S3	3.87	81	0.31	0.97	6.67	82	0.36	0.87
S4	2.22	102	0.04	0.27	5.27	78	0.59	0.78
S5	4.10	75	0.44	0.99	7.37	84	0.46	0.99
S6	4.03	93	0.14	0.68	6.83	95	0.15	0.55
S7	3.55	78	0.38	0.95	6.51	80	0.60	0.86
S8	3.27	82	0.29	0.95	7.34	89	0.33	0.90

[a] Percent sorbed during the initial phase (1 h) with respect to the sorbed amount at 24 h.

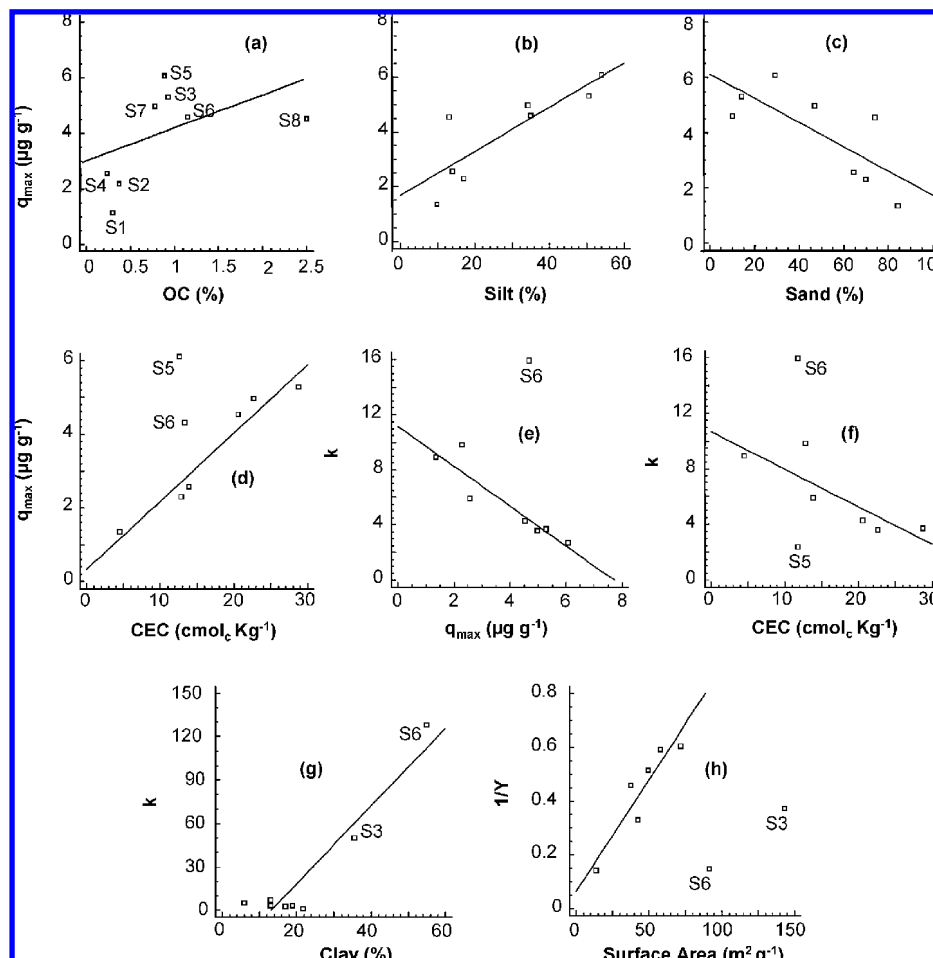**Figure 4.** (**a**, **b**, **c**, **d**, **e**, and **f**) Relationship between pseudosecond-order sorption parameters of imidacloprid and soil properties. (**g**) Relationship between pseudosecond-order kinetic reaction rate of diuron and clay content. (**h**) Relationship between slow sorption rate of diuron in Elovich model and surface area.

for imidacloprid (**Figure 4e**) when clay soil S6 was omitted ($r = 0.92$, $P < 0.01$). Furthermore, k values for imidacloprid also inversely correlated with the CEC of the soils except for S5 and S6 soils ($r = 0.85$; $P < 0.05$) (**Figure 4f**).

Unlike imidacloprid, no relationship was found between q_{max} values for diuron and soil properties. However, for both agrochemicals, the lowest q_{max} value corresponded to the loamy sand soil S1 with the lowest OC. The higher q_{max} value corresponded to the silt loam soil S5, which did not have the highest OC (**Table 1**). Despite the fact that the literature describes that soil organic carbon chemistry plays a major role in determining pesticide affinity (*28, 29*), our results reveal that soil OC content cannot by itself explain the sorption behavior of these assayed pesticides.

Values of k for diuron showed small variations among soils with low clay content (**Table 2** and **Figure 4g**) except in soils S3 and S6, with k values much higher than could be attributed to their higher clay content and surface area (**Table 1**). A close correlation ($r = 0.94$; $P < 0.01$) was observed between the sorption rate constant k for diuron and the soil clay content (**Figure 4g**).

Since the results of this model point to different sorption mechanisms for both pesticides depending on soil properties, other kinetic models were used to study the different sorption phases or mechanisms that control their sorption kinetics.

Elovich Equation. This model did not explain the experimental sorption kinetic for imidacloprid in sandy soil S4 and in clay soil S6 ($R^2 < 0.75$) because the sorbed rates at the initial
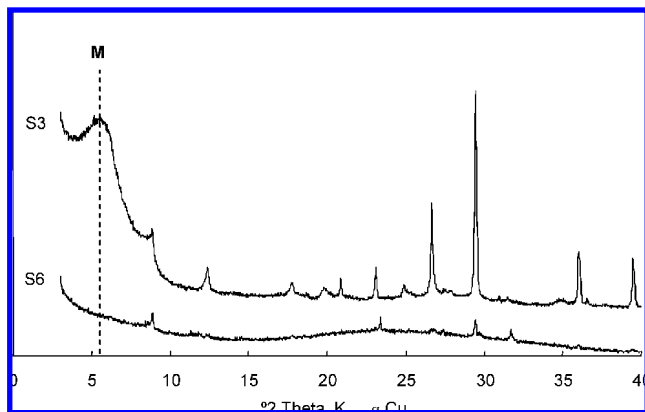
Figure 5. X-ray diffractograms of the clay fractions in oriented mount of soils S3 and S6 (M = montmorillonite).

stage (1 h) were higher than 90% (**Table 3**). This correlates with the straight line for soil S4 with a longer solid−solution contact time (**Figure 2**). However, in clay soil S6 with moderate OC content, there was a slight increment at the initial sorption stage, indicating a different sorption mechanism for imidacloprid for this clay soil. Soils with $R^2 > 0.75$ sorbed lower amounts of this insecticide at the initial sorption stage (75%−87%), pointing to additional sorption during the solid−solution contact time, which could be related to OC content and the clay mineral component of these soils (*30*). X-ray diffraction analysis of clay soils (**Figure 5**) revealed a higher smectite content in soil S3 than in soil S6. These swelling clays could explain the higher values for q_{max} and k in soil S3 compared to clay soil S6 and possibly a different sorption mechanism for this polar molecule in these clay soils.

In the case of diuron, the lowest R^2 values in Elovich adjustment correspond to the sandy and clay soils, S1 and S6, with sorption rates of close to 100% in the initial phase. In soils with better fit ($R^2 > 0.78$), the amount of herbicide sorbed during the fast phase concurred with data produced by Inoue et al. (*6*).

In general, Elovich coefficient (1/Y) values for imidacloprid were lower than those obtained for diuron (**Table 3**) and much lower for S1, S2, and S4 soils with lower OC content (**Table 1**). The plotting of 1/Y values for diuron against soil surface area (**Figure 4h**) reveals a significant correlation when the silty clay soil S3 and the clay soil S6 were omitted ($r = 0.93$; $P < 0.01$). Thus, the nature of the soil surface seems to play an important role in the second stage of the sorption kinetic for diuron.

Finally, to confirm if intraparticle diffusion is the sorption rate controlling stage, the Weber and Morris model was applied (*31*).

Weber and Morris Model. This model has been widely used to investigate sorption kinetics of inorganic and organic compounds by different sorbents (*32*) but has hardly ever been applied to pesticides. According to this model, plotting q against $t^{1/2}$ should produce a straight line with a slope k and pass through the origin when the intraparticle diffusion process controls the sorption mechanism. Values for intercept C give an idea of the thickness of the boundary layer, meaning that the larger the C values, the greater the boundary layer effect (*33*).

Kinetic parameters, given in **Table 4**, show a straight line in the case of the sorption of imidacloprid by S3, S5, S7, and S8 soils, but the intercept C does not go through the origin (**Figure 6a**). Thus, contrary to what would be expected for a well-agitated batch system, the boundary layer surrounding the particles has an important effect on the initial sorption kinetics

Table 4. Weber−Morris Model Parameters for Imidacloprid and Diuron and Their Respective Determination Coefficients (R^2)

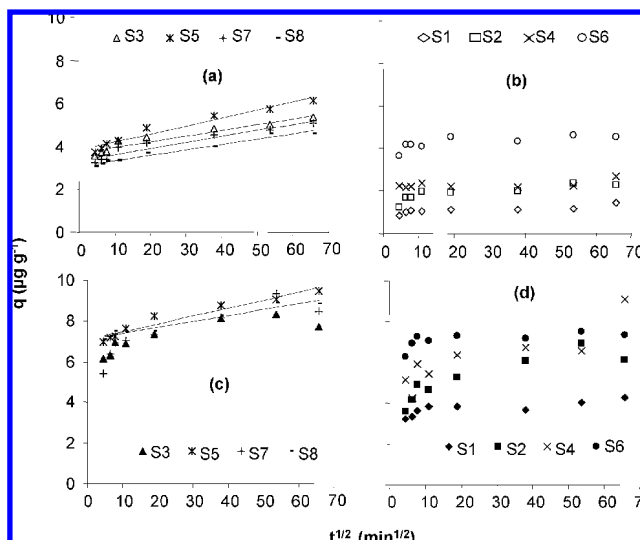| soil	imidacloprid			diuron		
	C (μg g^{-1})	k (μg g^{-1} min$^{-0.5}$)	R^2	C (μg g^{-1})	k (μg g^{-1} min$^{-0.5}$)	R^2
S1	0.94	0.006	0.75	3.43	0.012	0.67
S2	0.16	0.013	0.71	4.15	0.041	0.77
S3	3.68	0.026	0.91	6.50	0.028	0.69
S4	2.17	0.005	0.41	4.82	0.053	0.76
S5	3.81	0.037	0.95	7.08	0.039	0.94
S6	4.01	0.010	0.57	6.86	0.010	0.37
S7	3.35	0.028	0.90	6.20	0.046	0.78
S8	3.07	0.025	0.97	7.09	0.029	0.95

Figure 6. Weber and Morris plots for imidacloprid (**a** and **b**) and diuron (**c** and **d**) for the eight soils.

of this insecticide (*27*). The initial curved portion in the graph's shape for sandy soil samples S1 and S2 indicates an external mass transfer of the insecticide from the bulk solution to the soil particle surface (**Figure 6b**). As was observed with the Elovich, sorption data remained almost constant from the beginning in the case of S4 and S6 soils and indicate that imidacloprid sorption should take place in one phase.

The Weber−Morris parameters for the diuron sorption kinetic (**Table 4**, **Figure 6c** and **d**) follow a straight line for soils S5 and S8 ($R^2 > 0.94$). For the rest of the soils, the initial curved portion was more apparent for diuron than for imidacloprid, indicating a comparatively more important boundary layer effect surrounding the particles for diuron.

Finally, the anomalous data at the last time for S4 (**Figure 2**) could be related with degradation processes, although it was not detected in the control samples.

DISCUSSION

The lack of fit observed in the hyperbolic model after a solid−solution contact time of more than 24 h was also described by Grébil et al. (*13*) in the final stage of the sorption kinetic for tebutam in soil. This equation is therefore not useful to explain sorption of diuron or imidacloprid in soil over a long solid−solution contact time. By contrast, the pseudosecond-order kinetic equation was able to describe all sorption kinetics satisfactorily for both agrochemicals. However, different sorption processes seem to be involved in the overall reaction, as was indicated by the different models assayed.

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The lack of correlation of q_{max} for imidacloprid and diuron with OC content could be attributed to the low OC values for the soils studied (**Table 1**). These low values are frequently found in soils from southeast Europe (*16*). For this reason, other soil properties, usually masked by OC content, can play an important role in sorption dynamics.

The correlations found between q_{max} for imidacloprid with silt and sand content (**Figure 4b** and **4c**) revealed the relative importance of the exposed surface to the soil particles in the sorption process. Moreover, q_{max} and sorption reaction rate k for imidacloprid were related to the CEC of the soils, except for soils S5 and S6. Cox et al. (*30*) suggested that imidacloprid can be protonated at the soil surface in the -NH group of the imidazol ring and then be sorbed by cation exchange. This sorption mechanism will take place more easily in soils with low pH values (S2, S4, S7, and S8). At normal soil pH levels (S1 and S3), only small amounts of imidacloprid cation would be present at a given time but would be continually produced to retain equilibrium as it is sorbed. Kagabu and Matsuno (*34*) stated that the imidazolidine nitrogen of imidacloprid should be partially positively charged due to the force of a neighboring electron-withdrawing group such as nitroimine. Imidacloprid can also produce hydrogen-bonding or ion−dipole interactions with water or ions (Ca^{2+}, K^+) in the montmorillonites of S3 (**Figure 5**) through the -NO_2 group (*35*). However, its chloro-pyridine component was said to be capable of participating in the hydrogen-bonding process (*34*). In addition, the intraparticle diffusion observed in the Weber and Morris model for soil S3 can be related not only to OC content but also to its expanding clay minerals.

The noncorrelated values of q_{max} and k for imidacloprid in soils S5 and S6 (**Figure 4d** and **4f**) show a different sorption behavior pattern due to their intrinsic properties. Because the silt loam soil S5 is composed of larger aggregates or particles, the reaction rate of the total sorption process will decrease with increasing aggregate size, while its larger sorption capacity may be due to the nature of the particles and OC. However, the sorption behavior of soil S6 can be explained by the high clay content.

The inverse relationship between q_{max} and k for imidacloprid (**Figure 4e**) indicates a slower sorption rate in soils with higher OC content (S3, S5, S7, and S8). It is in these soils that the Weber and Morris model demonstrates intraparticle diffusion processes. In sandy soils S1, S2, and S4, showing the lowest OC content, there is a relatively high reaction rate using the pseudosecond-order kinetic method (**Table 2**). In soil S4, this high reaction rate is in line with the Elovich results, where a high sorption value was observed in the first sorption stage. However, in soils S1 and S2, this sorption kinetic is slower because of the mass transfer process or molecule diffusion described in the Weber and Morris model (**Figure 6b**). The variation in the sorption behavior of soil S8 is attributed to the nature of the OC, which could be due to variations in soil conditions (temperature, humidity, etc.) as a consequence of the different weather conditions in northern Spain (*36*).

The Elovich equation and Weber−Morris model in soils S3, S5, S7, and S8 (**Tables 3** and **4**, and **Figure 6a**) confirmed the existence of a slow diffusion of these insecticide molecules to less accessible sites in soil with OC values of around 1%. A second imidacloprid sorption stage was also observed in similar soils (*11*).

In the case of diuron, important differences in the sorption kinetics were found compared with that for imidacloprid becaue of its chemical properties. The higher hydrophobicity of diuron

($K_{ow} = 700$) compared with that of imidacloprid ($K_{ow} = 3.24$) and its higher affinity with OC greatly increases its sorption rate (*29*). Ahmad et al. (*37*) showed that rather than soil OC content, aromacity was a strong determinant of pesticide sorption in soil, which could partly explain the lack of correlation between OC content and sorption of diuron.

The high clay content, corresponding to a larger surface area, in soils S3 and S6, could explain the very high reaction rate constants of diuron in these soils (**Table 2**, **Figure 4g**). Nevertheless, unlike the case of imidacloprid, the type of clay did not affect the maximum amount sorbed. Furthermore, we can ignore the fact that these clay soils had a comparatively higher OC content compared to soils S4, S5, and S7, although the maximum amounts sorbed (q_{max}) were lower. This reduction in the affinity of the organic matter with diuron in these clay soils could be related to a reduction in the sorption sites available due to organic matter−clay interactions. In addition, in case of soil S6, the $CaCO_3$ content (**Table 1**) could negatively affect the sorption efficiency of diuron by the soil OC (*24*). All these factors could explain the lack of correlation between the soil OC content and the maximum amount sorbed.

In sandy soils S1 and S2, the limited amount of diuron retained must be due to having the lowest OC levels and their high sand content. Regitano et al. (*38*) also observed that sandy soil with low OC content had fewer available sites to promote chlorotalonyl sorption.

The Elovich equation revealed a sorption kinetic for diuron in a single stage in soils S1 and S6 (**Table 3**). Because these soils have very different properties, it is difficult to attribute this sorption behavior to a specific soil property. Kookana et al. (*39*) stated that sorption in the initial stage takes place in reaction areas that depend on the types of soil and the accessibility of the pesticide molecule to them. Consequently, the high accessibility of diuron in soil S1 and its low sorption capacity could explain sorption in a single stage. In soil S6, the nature of the soil surface due to clays and OC enhances the sorption rate, as has already been observed with the pseudo-second-order kinetics (**Figure 4g**), which carries out sorption in one initial stage. The Weber and Morris model showed an important boundary layer effect for diuron and pointed out that the partition of this molecule also has a major influence on the initial sorption stage.

Finally, we can ignore the fact that the shaking conditions in the batch method could mask the effect of soil properties, enhancing sorption at the fast rate and underestimating the diffusion effect in the slow phase (*6*).

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